

Identification of the Parasitic Chemical Reactions during AlGaN OMVPE

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Motivation—GaN and AlGaN alloys are extremely important materials with widespread applications for optoelectronics (e.g. solid state lighting) and high power electronics. Organometallic vapor phase epitaxy (OMVPE) is the primary deposition methodology, but it suffers from several growth chemistry anomalies. Growth rate and alloy composition are often a sensitive function of temperature and other reactor variables. These factors make the AlGaN OMVPE process difficult to control and increase the cost of the material. Conventional wisdom has been that the non-ideal OMVPE behavior is due to parasitic “pre-reactions” between the reactants, but these processes have not been studied in a reliable and thorough manner. An important question is whether the parasitic processes occur at low temperatures (e.g. near the inlet, $<100^{\circ}\text{C}$) or require high temperatures (e.g. near the wafer, $\sim 1000^{\circ}\text{C}$).

Accomplishment—We have explored many possible mechanisms for the parasitic pathways using both experimental techniques and complex reactive flow simulations. As expected, trimethylgallium (TMGa) and trimethylaluminum (TMAI) react with ammonia to form adducts, which we have unambiguously identified with mass spectroscopy and FTIR. We have measured the vapor pressure of the adducts near room temperature and found that physical condensation can be an important process, especially at higher reactor pressures and higher reactant concentrations. However, over the 0– 100°C range we have found no evidence of significant irreversible decomposition reactions, such as methane elimination (see Fig. 1), which have often been postulated to be the source of the loss of group-III flux. The TMAI: NH_3 adduct does irreversibly react to form CH_4 , but this process only becomes detectable above

125°C .

We have modified one of our research rotating disk reactors (RDR) so that TMGa, TMAI, and NH_3 are premixed before entering the chamber. Growth rates in this RDR are comparable to the growth rates from our RDR where the group-III precursors are kept separate from NH_3 at the inlet. We have measured growth rates over a wide range of operating conditions and concluded that the parasitic reactions must be occurring in the thermal boundary layer just above the wafer. One example of this type of experiment is the growth rate dependence on spin rate (Ω) shown in Fig. 2. Lowering Ω increases the residence time in the boundary layer, which allows the parasitic processes to advance to a greater extent, thus dropping the growth rate. If there were no parasitic loss terms the growth rates would be independent of Ω and at the transport limit. A low temperature mechanism would not exhibit the strong Ω dependence observed. Many details of the high temperature parasitic mechanisms still need to be resolved, but our current working hypothesis is based on homolysis of TMGa and TMAI, followed by gas-phase association reactions (e.g. particle nucleation).

Significance—By showing that the parasitic mechanism requires high-temperatures we were able to use a reactor design with premixed gases. Premixing eliminates a major source of nonuniformity in the system. By understanding the details of the high-temperature parasitic mechanism we will be able to optimize the AlGaN OMVPE process. We have already found that for GaN we can reach the transport limit by increasing the spin rate (Fig. 2).

Sponsors for various phases of this work include: BES, LDRD

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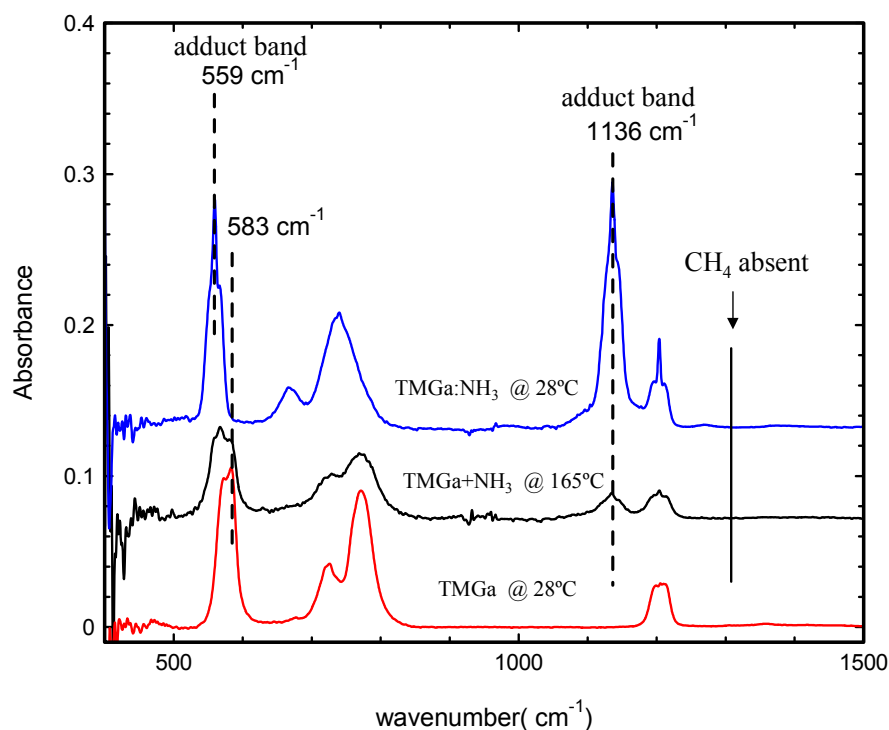


Figure 1. Gas-phase FTIR demonstrates that for typical OMVPE inlet conditions the TMGa:NH₃ adduct formation is reversible, i.e. no CH₄ is produced. As the temperature is raised this adduct simply dissociates back into the original reactants.

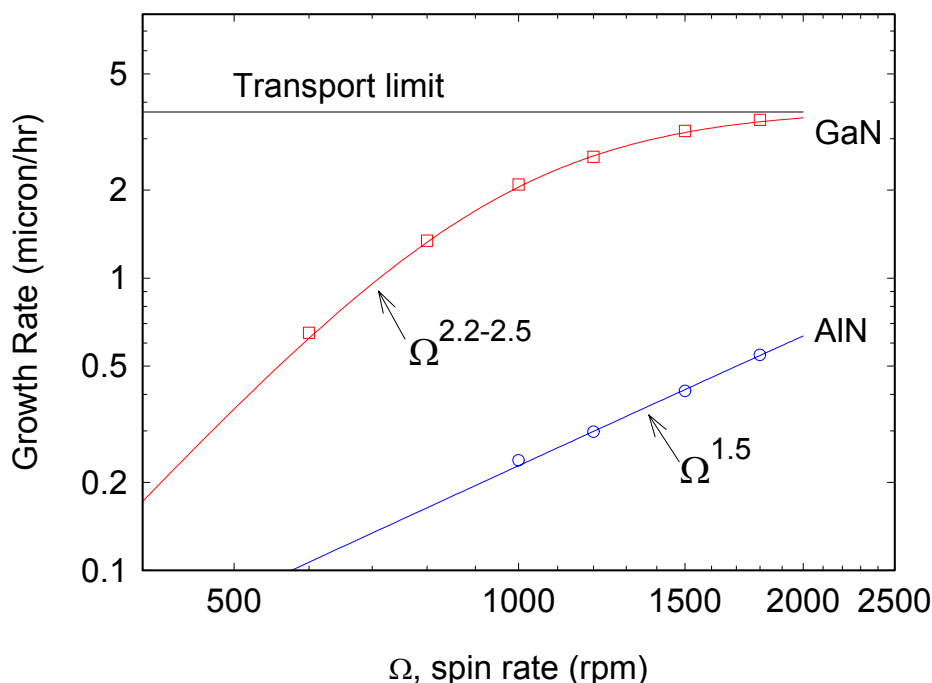


Figure 2. Growth rate of GaN and AlN at 1050°C as a function of RDR spin rate (Ω) at matched flow conditions. Without a parasitic process the growth rate would be independent of Ω and at the transport limit. A high-temperature parasitic chemical mechanism is responsible for the strong Ω dependence.